

The Precise Lattice Constant and the Expansion Coefficient of Chromium between +10 and +60° C.

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The constants of pure, sintered, electrolytic chromium were determined by the powder method over a range of +10 to +60° C., using copper radiation; and a value of 2.87918 ± 0.00004 kX. or 2.8850 ± 0.0001 Å at 20.0° C. was obtained. The refraction correction of +0.00006 is added to the constants. The error limits given include random as well as systematic errors. The precision of the determinations themselves (with systematic errors excluded) was between 1:200,000 and 1:400,000. The expansivity curve of chromium, showing a slight break at +32.5° C., could be described by two expansion coefficients $\alpha = 7.47 \times 10^{-6}$ above, and 4.4×10^{-6} (°C.)⁻¹ below, the transition point. The average expansion coefficient of the samples agreed with that determined by Hidnert.

Introduction

Considerable effort has been expended during the past thirty years to determine the lattice constant and the expansion coefficient of chromium. However, the purity of the chromium used was in most cases not of the highest grade, and the results did not agree very well. The best values obtained in recent years are summarized in Table 1.

Table 1. *Lattice constant of chromium*
(Cr radiation)

Authors	Temperature (°C.)	<i>a</i> (kX.)
Wood (1937)	18	2.8796
Fine, Greiner & Ellis (1951 <i>a, b</i>)	20	2.8790
Taylor & Floyd (1952)	20	2.8784, 2.8785
Pearson & Hume-Rothery (1953)	18	2.8787

MacNair determined the thermal expansivity of chromium by means of an interferometric dilatometer (Nix & MacNair, 1941), with the result that near 38° C. there is a break in the expansivity curve. Fine, Greiner & Ellis (1951*a, b*) found discontinuous changes in Young's modulus, internal friction, electrical resistivity, and thermoelectric power, all near 37° C.; although no definite break in the thermal expansion curve, as determined by X-rays, could be found. An inflection point just below +35° C. in the resistance-temperature curve was reported by Sully, Brandes & Mitchell (1952-3*a, b*).

The linear thermal expansion coefficient was determined by Disch (1921), Chevenard (1922*a, b*), Hidnert (1941), and Fine *et al.* (1951*a, b*), with their results showing great variations. Hidnert obtained expansion coefficients between 5.7 and 6.66×10^{-6} in the interval of 20-60° C. for 99.3 and 98.7% pure chromium, and contrary to Nix & MacNair (1941) he did not observe breaks in the smooth expansion curves.

The purpose of the present investigation was to check the expansion coefficient of chromium once more with X-rays, and to determine the exact lattice parameter of the metal. As extreme precision was necessary for such measurements, copper radiation was used, which yielded a strong interference under a Bragg angle of 87.4°, and which was also used by Frohnmeyer (1951) and by Frohnmeyer & Glocker (1953) in their studies.

The chromium used and the experimental procedure

The sharpest powder lines were produced by mounts of sintered electrolytic chromium (of the C. Hardy Inc.), which contained as impurities:

H: 0.0001, O: 0.0088, N: 0.019, C: 0.005, Sb: 0.01% by weight.

Small quantities of the metal were ground in agate mortars, the powder was then sieved through a 325 mesh screen by shaking the screen slightly, and the fine powder that passed the sieve was placed in a silica glass bulb which was evacuated while being heated, then sealed off. Next, the bulb was heated at 850° C. for 2½ hr. to expel the remainder of the gasses dissolved in the chromium powder, and to recrystallize the highly deformed metal leaflets. A longer time for heating or a higher temperature could not be applied because then the grain size became so coarse that the powder produced spots on the X-ray powder diagrams.

The exact value of the lattice constant of the powder was calculated from patterns obtained in precision cameras of 64 mm. diameter, the sample and the camera having a constant temperature. The constancy of the temperature was maintained within limits of

$\pm 0.05^\circ \text{C}$. by placing the camera in a special thermostat for a few hours previous to the exposure. The temperature was controlled by circulating water from a thermostatic bath, as previously described (Straumanis, 1949, 1953; Straumanis & Aka, 1952; Klug & Alexander, 1954, pp. 454–61). The exposures were mainly made at 10° intervals between 10 and 60°C . For measuring the films, which were 18 cm. in length, a comparator accurate to 0.001 mm . was used. The bare films were inserted into the camera in the asymmetric position so that no correction for film shrinkage nor comparison with a standard substance was necessary. The absolute value of the lattice constant was computed directly from the Bragg angle obtained from the measurement of the films without application of any analytical or graphical extrapolation method. The powder mounts were as thin as possible, 0.12 – 0.2 mm . in diameter (Straumanis, 1949, 1953; Straumanis & Aka, 1952; Klug & Alexander, 1954).

Copper radiation ($\lambda K\alpha_1 = 1.537395 \text{ kX}$.) yielded the strong α_1 line No. 14 (indices 321, Straumanis, 1952) under a Bragg angle of 87.36° (at 30.9°C .) Unfortunately, this radiation excited a fluorescent radiation in the chromium sample which darkened the film, especially in the back-reflection region. By placing a piece of 0.035 mm . thick aluminum foil directly on the film, so that it covered the 321 α_1 ring, the fluorescent radiation could be greatly absorbed at this point. Nevertheless, the last 321 α_1 line was so strong, even with a collimator aperture of 0.6 mm ., that only a 30 min. exposure was necessary to produce a film with distinct lines. The measurement of the front-reflection lines (for the determination of the circumference of the film) was not much affected by the fluorescent radiation. To obtain uniformly blackened lines, scanning (Straumanis & Aka, 1951), because of the small aperture of the collimator, in addition to rotation of the sample, was necessary. As the back-reflection diffraction ring (No. 14) was very close to the 2 mm . hole in the film, the hole was never punched but carefully bored with a special, sharp, drill bit to prevent deformation of the film (after development and drying) and subsequent distortion of the diffraction ring (Jelinek, 1949). Because of the very

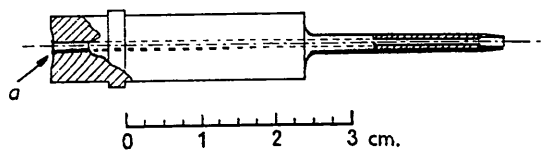


Fig. 1. Collimator for a 64 mm. precision camera which permits obtaining Bragg angles up to 88° . *a*: hypodermic needle with a bore of 0.6 mm .

large diffraction angle the hole for the collimator could not be wider than 2 mm . Thus, a special collimator had to be constructed for the camera (Fig. 1).

Lattice parameter and expansion coefficients of chromium

The results in the form of an expansivity curve over a range of 50°C . are shown in Fig. 2. Each point of

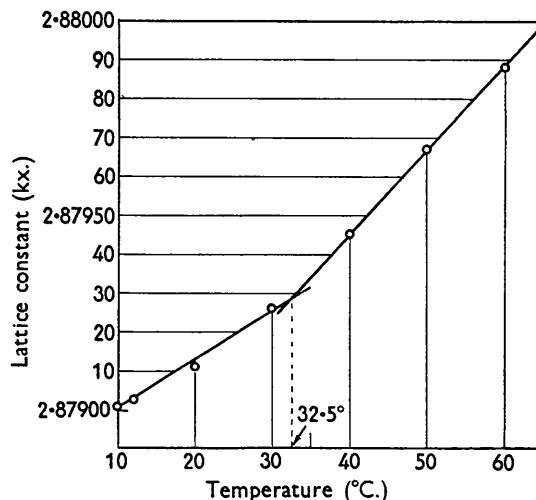


Fig. 2. Lattice constant of sintered electrolytic chromium versus temperature.

the curve represents an average value of the constant as calculated from 2–6 films. It was preferred to draw two straight lines through the experimented points, thus arriving at a slight break in the curve at 32.5°C . Hence the linear expansion coefficients for both branches of the curve could be calculated from the expression

$$\alpha = \frac{1}{a} \frac{\Delta a}{\Delta t}, \quad (1)$$

t being the temperature (in deg. C.) and a the lattice parameter. The mean values of α obtained were:

$$\alpha_l = 4.4 \times 10^{-6} (\text{°C.})^{-1} \text{ (for the lower part of the curve up to } 32.5^\circ \text{C.) ,}$$

and

$$\alpha_u = 7.47 \times 10^{-6} (\text{°C.})^{-1} \text{ for the upper part of the curve.}$$

Using these expansion coefficients, the values of the constants obtained at different temperatures were reduced to one single temperature, e.g. to 32.5°C ., and the accuracy of the lattice-parameter determinations (Table 2) was checked.

The probable error (or the standard deviation, Wilks, 1951) shows that the reproducibility of these measurements is better than $1:400,000$, an exceptional precision which was also attained with germanium (Straumanis & Aka, 1952). This high precision is the result of: (1) the application of the high Bragg angle of more than 87° ; (2) the constancy of the temperature of the sample ($\pm 0.05^\circ \text{C}$.); and (3) the improved experimental technique used. Of these three reasons the first is the decisive one; at Bragg angles approaching

Table 2. *Lattice constant of sintered electrolytic chromium reduced from the temperature of the measurement to 32.5° C. and 20° C.*

(Cu radiation)			
t (°C.)	a_t (kX.)	$a_{32.5^\circ\text{C.}}$ (kX.)	$a_{20^\circ\text{C.}}$ (kX.)
60.0	2.879883	2.879291	—
50.0	665	89	—
40.0	453	92	—
30.0	260	92	2.87913
20.0	108	67	1
12.0	021	82	2
10.0	007	93	3
Mean of all measurements		2.879287	2.879123
Probable error		± 0.000006	± 0.000007

90° the variation of $\sin \theta$ with θ itself is very small. Thus, fairly large mistakes can be made in measuring the positions of the lines without any appreciable effect on $\sin \theta$. However, the precision as reported in Table 1 refers only to the method of measurement, disregarding the systematic errors. The error limits of the absolute value of the lattice parameter can be estimated only by a discussion of errors.

Discussion of errors

Using the same specimens of sintered electrolytic chromium, and making the exposures at constant temperatures (within $\pm 0.05^\circ\text{C.}$) of the samples, the only variable of the Bragg equation which changes with temperature is the reflection angle θ . Hence, keeping the temperature constant, the accuracy of determination Δa of the lattice constant a can be determined by the logarithmic differentiation of the Bragg equation:

$$\Delta a/a = -\cotg \theta \Delta \theta. \quad (2)$$

In order to determine the standard deviation $\Delta \theta$ from all the 18 films evaluated (none was discarded), but obtained at different temperatures of the powder mounts (the angles varied from 87.106° at 60°C. to 87.474° at 10°C.), the θ angles measured were reduced to one temperature of 32.5°C. The reduction was made using the relation $(\theta_1 - \theta_2)/(t_2 - t_1)$, computed from the experimental data. Then from the 18 reduced values the standard deviation $\Delta \theta$ was calculated: $\Delta \theta = \pm 0.00627^\circ$. Substituting this value for $\Delta \theta$ in (2), at an angle $\theta = 87.40^\circ$,

$$\Delta a = \pm 4.93 \times 10^{-6} a \quad (3)$$

was obtained, which means a precision of 1:203,000 in the case of chromium. The error due to the inaccuracy of temperature readings ($\pm 0.05^\circ\text{C.}$) can be computed from (1) and the two expansion coefficients α_l and α_u :

$$\begin{aligned} \Delta \alpha_l &= \pm 2.2 \times 10^{-7} a, \\ \Delta \alpha_u &= \pm 3.7 \times 10^{-7} a. \end{aligned}$$

The absorption correction* Δa_{ab} , is even smaller:

$$\Delta a_{\text{ab}} = \pm 9 \times 10^{-8} a.$$

The other corrections due to the inaccuracy of the camera also vanish with the high angle of reflection. Thus all these errors and corrections are well within the error limits as given by (3), and the accuracy of the lattice-constant determination is limited only by the angular measurements. The latter gave a theoretical accuracy of at least 1:200,000, which is, however, only half as good as the practically attained value of 1:400,000. A more thorough treatment would give a higher theoretical accuracy.

This all refers to the accuracy of the method itself, using samples of the same chromium preparation and disregarding the systematic errors. If the purity of the sample, the inaccuracy in the determination of X-ray wavelength $\Delta \lambda$, and the error Δc with which the conversion factor ($\lambda g/\lambda s = c$) is affected, are taken into account, the accuracy of determination of the a constant itself in kX., or of the absolute value a_0 in Å can be computed by (4) as the other values of the Bragg equation are constants:

$$\frac{\Delta a_0}{a_0} = \left[\left(f_1 \frac{\Delta c}{c} \right)^2 + \left(f_2 \frac{\Delta \lambda}{\lambda} \right)^2 + (-f_3 \cotg \theta \Delta \theta)^2 \right]^{\frac{1}{2}} \quad (4)$$

The values for the relative errors are:

$$\Delta c/c = \pm 3 \times 10^{-5} \text{ (Lonsdale, 1950);}$$

$$\Delta \lambda/\lambda = \pm 3.25 \times 10^{-6} \text{ (for Cu } K\alpha_1\text{);}$$

and

$$\Delta a/a \pm 4.93 \times 10^{-6}$$

(for the 3rd expression see (2) and (3)). The comparison of the values of the two last expressions show that the precision with which the lattice parameter of chromium was determined is close to the precision of the best X-ray wavelength determinations (Cu $K\alpha_1$). f_1, f_2 and f_3 are safety factors, each of them larger than 1. The necessity of these factors follows from the consideration that relative errors are accidental or random errors; they reflect the quality of the measurements, but they do not contain the *systematic* error, which is undoubtedly in any measurement, and which may even be several times as large as the accidental error. It is the task of the investigator to estimate the value of the factor f for each kind of measurement, so that the systematic error becomes *included* in the deviation. f_1 is assumed to be $\sqrt{2}$ because, according to DuMond & Cohen (1952a, b), c is 1.002063 instead of the accepted 1.00202. To cover the first value, the error ± 0.00003 has to be increased by the factor $f_1 = \sqrt{2}$. It is also assumed that $f_2 = \sqrt{2}$ covers the systematic errors in Siegbahn's measurements of the Cu $K\alpha_1$ line. As the chromium used was not of the highest purity, the systematic error induced by the impurities may be

* Computed using equation (2) and equation 18A, p. 404 of M. J. Buerger's *X-ray Crystallography* (1942).

Table 3. Lattice parameters a and a_0 of pure sintered electrolytic chromium at 20° C. and values of the accidental and total errors

	Error (kX. or Å)	Accuracy	a or a_0
Probable error of the direct measurement	± 0.000007	1 : 400,000	2.87912 ₃ kX.
Probable error calculated	± 0.000014	1 : 200,000	2.87912 kX.
Systematic error included (a in kX.)	$\pm 0.00004_4$	1 : 60,000	2.87912 kX.
Systematic error included (a in Å)	± 0.00013	1 : 22,000	2.8849 ₄ Å
Refraction correction			+0.00006

included in the measurements if $f_3 = 3$. Under such conditions the probable errors involved in the lattice-constant determinations can be calculated equally well when expressed in kX. ($f_1 = 0$), or in Å (equation (4)). The results, together with the values of the lattice constant (see Table 2), are given in Table 3.

Wilson (1940) has shown that the true lattice spacing of a cubic crystalline powder is obtained by increasing the calculated lattice spacing by a fraction $(1-\mu)$ of itself (μ being the index of refraction). According to Klug & Alexander (1954, pp. 98-100) this can be written in a form

$$a_{\text{corr.}} = a_{\text{obs.}} \times (1 + \delta), \quad (5)$$

where $\delta = 1-\mu$. The latter can be calculated for a certain substance from the dispersion equation (e.g. Lindh, 1930; Klug & Alexander, 1954, pp. 98-100). Applying (5) for the computation of the refraction correction for chromium (density = 7.2 g.cm.⁻³) with copper radiation, a correction of 6.1×10^{-5} was obtained, which agreed very well with 6.4×10^{-5} calculated from the Ewald equation (Lindh, 1930) applicable to single crystals. Barrett (1952) recommended, on the basis of a qualitative proof only (without however disproving the conclusion of Wilson) omitting the refraction correction in the case of powders. The correction mentioned in Table 3 has to be added to the results.

Conclusion

Application of copper radiation permitted a very high precision to be attained in the lattice-constant determination of chromium, and hence the establishment of a transition point in the expansivity curve in the form of a slight break at 32.5° C., which agrees fairly well with that of 37° C. found by Fine *et al.* (1951a, b) by an interferometric dilatometer. The agreement is much better with the point at less than 35° C. found by Sully *et al.* (1952-3a, b) by electrical resistance measurements. The expansion coefficient of 7.47×10^{-6} above 32.5° agrees fairly well with that one established by Hidnert (1941) ($5.7-6.6$ or 7.5×10^{-6} up to 100° C.), but below the break the coefficient is lower (only 4.4×10^{-6}). However, the average expansion coefficient, 5.94×10^{-6} , agrees well with those of Hidnert. The reason why the inflection point was not observed by Hidnert may lie in the insufficient degassing of the sample.

It is very difficult to reproduce the expansion coefficient α accurately, even with the same sample, if extreme precision is not used. This may be the reason it is sometimes found that certain cubic metals may not be precisely cubic through a range of temperatures below their melting point (Kochanovská, 1949). Although chromium in its thermal expansion showed a discontinuity at 32.5° C., there were no signs of abnormal broadening of the lines, nor of other alterations in the powder patterns with increasing temperature (up to 60° C. at least). A line broadening should be expected as soon as the cubic crystal begins to change its symmetry. The results on chromium are in agreement with the measurements of Eppelsheimer & Penman (1952) on copper, and with Batchelder & Raeuchle (1954) on nickel and iron, both of whom found no thermal anisotropy of dilation of the metals mentioned, despite previous assertions to the contrary (Kochanovská, 1949).

The lattice constant of chromium is somewhat larger than those previously obtained (Table 1), presumably because of the higher-purity material used, but agrees with the constants of the earlier authors within the error limits given by them.

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X-ray Scattering by Neutron-Irradiated Single Crystals of Boron Carbide. I

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Neutron irradiation of single crystals of boron carbide produces very strong X-ray diffraction effects. These effects are (a) contraction of the lattice in the c_0 direction and expansion in the a_0 direction, (b) an anisotropic artificial temperature factor which is six times as strong in the c_0 direction as in the a_0 direction, (c) changes in the average lattice positions of a number of the atoms, and (d) very heavy diffuse scattering surrounding many of the reciprocal-lattice points. Annealing experiments show that most of the X-ray effects are removed in the temperature range of 700 to 900° C. The present work shows that the effects are due to the production of the anisotropic defect in the lattice. This defect is produced by the selective removal of the central carbon atom in a chain of three carbon atoms which lies parallel to the c_0 axis. In the 700–900° C. range the selectively removed carbon atom becomes mobile and finds its way back to its normal position. The effects are interpreted qualitatively in terms of an elastic model of Huang. Work is in progress to extend the analysis of Huang to the case of anisotropic defects and to measure and interpret the diffuse scattering in detail.

Introduction

The qualitative nature of the X-ray effects found in neutron-irradiated single crystals of boron carbide, B_4C , has been described recently (Tucker & Senio, 1954). These effects are (a) large, highly anisotropic lattice parameter changes, (b) a highly anisotropic artificial temperature factor, (c) true structural changes, and (d) very heavy diffuse scattering surrounding many of the reciprocal-lattice points. Items (a), (b) and (c) have been studied in detail, including annealing experiments, and are now well understood.

The results of these studies will be reported in the present paper, while detailed studies of the diffuse scattering will be given in a second paper.

The damaging reaction and the crystal structure of boron carbide

In most nuclear reactors, the radiation damage produced in boron carbide is overwhelmingly due to the reaction of the B-10 nucleus with thermal neutrons to form Li-7 and He-4 nuclei. According to Bethe (1950), these nuclei dissipate 0.84 and 1.47 MeV., respectively, in the lattice by ionization and bumping collisions. The effects of the B-10 reaction far outweigh those of fast neutron bumping collisions because

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